

**Residual Metallic Impurities within Carbon Nanotubes Play
Dominant Role in Supposedly “Metal-Free” Oxygen Reduction
Reaction**

Lu Wang, and Martin Pumera*

Supplementary Information

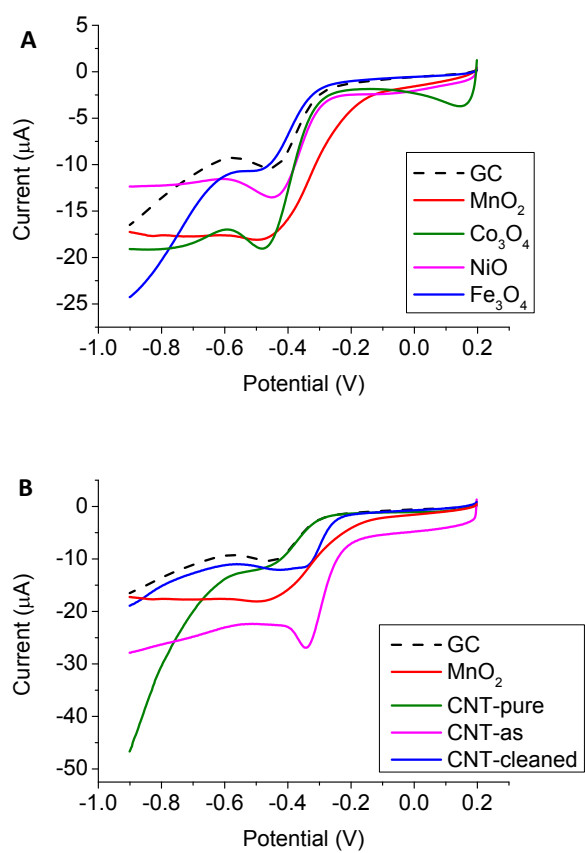


Figure S1. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and (A) GC electrode modified with Co_3O_4 (green line), NiO (magenta line), Fe_3O_4 (blue line), and MnO_2 (red line) nanoparticles. (B) GC electrode modified with MnO_2 (red line), CNT-as (magenta line), CNT-cleaned (blue line), CNT-pure (green line). Scan rate: 100 mV s^{-1} .

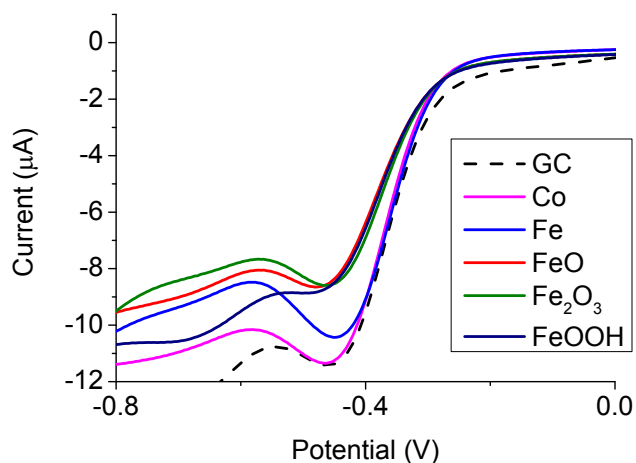


Figure S2. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and metal/metal oxide modified electrode. Scan rate: 100 mV s⁻¹.

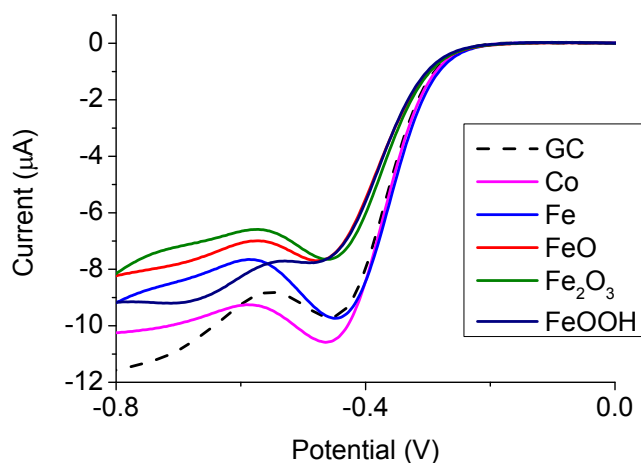


Figure S3. Linear sweep voltammograms recorded in air-saturated 0.1 M KOH solution using a bare glassy carbon electrode (black-dashed line) and metal/metal oxide modified electrode. After baseline correction. Scan rate: 100 mV s⁻¹.

Experimental section

Material. Multiwalled carbon nanotubes (CNT-as) (98%, -OH terminated, 5-15 nm/ 1-5 µm) were purchased from Bucky, USA. MnO₂ powder was purchased from Alfa Aesar. Fe, FeO, FeOOH, Fe₂O₃, Co, Co₃O₄, Fe₃O₄, NiO powders, N,N-dimethylformamide (DMF), and CNT-pure were

obtained from Sigma-Aldrich. Fe nanoparticles were from Nanoiron (Czech Republic). All CNTs had been extensively characterized previously (CNT-as contains 0.616 wt% of Co, 0.003 wt% of Fe, 0.015 wt% of Ni and 0.596 wt% of Mn; CNT-cleaned contains 0.02 wt% of Co, and 0.014 wt% of Mn). Glassy carbon electrode was obtained from Metrohm, Pt and Ag/AgCl (saturated) electrodes were purchased from CHI Instruments, TX, USA.

Apparatus. All voltammetric experiments were measured by using an electrochemical analyzer Autolab PGSTAT 101 (Ecochemie, Utrecht, The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Metrohm Autolab B. V.). The electrochemical measurements were performed by using a three-electrode configuration at room temperature. The GC electrode was used as the working electrode, platinum disk and an Ag/AgCl (saturated) electrodes were used as the auxiliary and reference electrode, respectively.

Purification of CNTs

CNTs purification was performed in a quartz glass reactor that equipped a magnetic manipulator at 1000 °C. 0.2 g of CNT-as was placed in a porous quartz glass capsule which was connected to a magnetic manipulator inside a vacuum tight quartz tube furnace with controlled atmosphere. In order to remove oxygen, the reactor was flushed with nitrogen by repeated evacuation of tube furnace and the evacuated reactor was filled with chlorine and CNT sample as quickly inserted by the magnetic manipulator to the preheated furnace. The sample was treated in a chlorine-nitrogen (1000 mL/min) atmosphere for 10 min. Then the treated CNT was removed from the hot zone of the reactor and three times evacuated and refilled with nitrogen in order to remove chlorine from the reactor.

Electrochemistry

All nanoparticles, CNTs were dispersed in DMF to prepare a 5mg/mL suspension for modification of the glassy carbon electrode. The GC electrode was cleaned by deionized (DI) water, and polished with a 0.05 μm alumina polishing cloth, and then cleaned by DI water again. The prepared suspensions were sonicated for 5 min and 1 μL of suspension was dropped by pipette onto the GC electrode and the dropped suspension was allowed to dry out at room temperature. All measurements were

performed in 0.1 M potassium hydroxide solution at 100 mV/s scan rate. Onset potential was determined as potential at 10% of the wave current.¹

¹ F. Maillard, A. Bonnefont, M. Chatenet, L. Guetaz, B. Doisneau-Cottignies, H. Roussel, U. Stimming, *Electrochim. Acta* 2007, 53, 811.